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New Jurassic amber outcrops from Lebanon

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Summary

Amber predating the Lower Cretaceous is extremely rare. During the past two decades, records of discoveries of amber sites have increased considerably worldwide. We report herein the discovery of ten new outcrops of amber from the Late Jurassic in Lebanon, in addition to other nine outcrops described by Azar et al. (2010). Some of these outcrops gave large centimetric sized amber pieces. Each of these new amber outcrops is described, and its infrared spectrum is given. Though the Jurassic amber yielded to date no more than some fungal inclusions, this discovery is significant and promising especially in the reconstruction of the paleoenvironment.

Keywords

Late Jurassic; Lebanon; FTIR; infrared spectrum

Introduction

Amber is a fossilized plant resin which is preserved throughout geological time (Langenheim, 1969). The complexity of the chemical composition of amber makes it unique considering the great preservation of biological inclusions in their 3D pristine and minute details (Langenheim, 2003). Its age ranges between a few millions and 320 million years (Mid Carboniferous) (Sargent Bray and Anderson, 2009). During the past two or three decades, the discoveries of amber outcrops have largely increased all over the world. There is no doubt that *Jurassic Park* in 1993, the famous American science fiction adventure thriller film directed by Steven Spielberg and based on the

novel of the same name by Michael Crichton, played a noticeable role in making amber more popular. Before this date, interest in amber was mainly restricted to Baltic and Caribbean countries, though amber occurrence was recognized from several localities worldwide.

Amber outcrops predating the Lower Cretaceous are scarce, and usually contain pieces of small millimetric sizes from Jurassic, Triassic and Carboniferous ages (Gianolla et al., 1998; Philippe et al., 2005; Roghi et al., 2006; Sargent Bray and Anderson, 2009; Azar et al., 2010; Schmidt et al., 2012).

After the recent discovery of some arthropods in Triassic amber from the Dolomites, Italy (Schmidt et al., 2012), the Lebanese Lower Cretaceous amber is no longer the oldest one with biological inclusions, but still very important for the study of arthropod evolution, as the period of its formation is contemporaneous with the appearance of flowering plants and the associated newly evolving ecosystems; it documents the initial diversification of the modern entomofauna and the disappearance of some archaic insect groups (Azar, 1997a, b, 2000, 2007; Azar and Nel, 1998; Azar, 2012; Poinar and Milki, 2001).

Azar et al. (2010) reported the discovery of nine Late Jurassic amber outcrops in Lebanon making it the second record of Jurassic amber after Thailand (Philippe et al., 2005). Jurassic amber was found also in Daohugou (a single droplet) in the Middle Jurassic during the field trip occasioned by the Fifth FossilX3 Conference in China (Azar pers. com.). Herein we report the discovery of ten more new Late Jurassic outcrops in Lebanon. The new outcrops are described, amber is characterized, and their infra-red spectra (Fourrier Transformed Infrared [FTIR]) are given.

Methods

Geological setting

All ten amber sites are located in the northern part of Mount Lebanon, as the sites described by Azar et al. (2010) (Fig. 1), in volcano-lateritic Late Jurassic deposits (volcanic Kimmeridgian, symbolized as β_{J_6}). The amber is found in lens of lignite mixed with laterites and pyrite that occupy pits in volcano-basaltic complex soil. During the Late Jurassic, and resulting from the active paleotectonic, there was volcanic and basaltic effusion, which created relief in shallow marine water, hence basaltic deposits were associated to the neritic sediments (Dubertret, 1945, 1947, 1950, 1951, 1955; Wetzel, 1945). The association of basalt and lignite, and the large distribution of basaltic deposits allowing the resin remains to accumulate are explained previously by Azar et al., (2010).

Jurassic amber outcrops

The Late Jurassic amber outcrops are described successively from South to North (Figs 1–20):

QARTABA: (34°5.676'N; 35°51.679'E); Mouhafazet Jabal Loubnan (Governorate of Mount Lebanon), Caza (District) Jbeil (Byblos), Central Lebanon. The outcrop

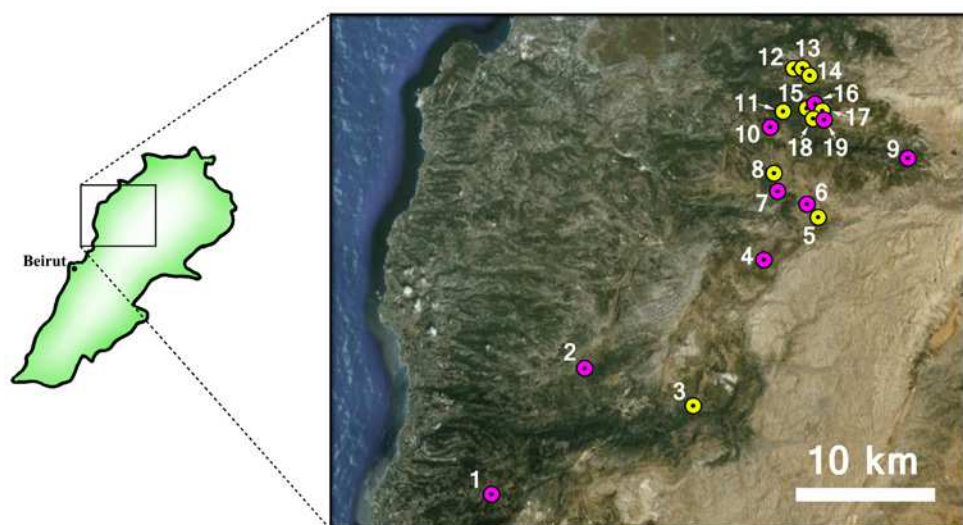


Figure 1. Map showing all the Late Jurassic amber localities in Lebanon. Pink dots represent sites described by Azar et al. (2010); yellow ones represent the newly discovered outcrops. 1: El-Ghineh; 2: Ehmej – Aalmat; 3: Qartaba; 4: Tannourine El-Faouqa; 5: Harissa; 6: Ed-Doueir; 7: Arz Tannourine; 8: Hadath El-Joubbeh; 9: Bcharreh – Beqaa Kafra; 10: Beit Mounzer; 11: Qnaouer; 12: Ehden (Mantra); 13: Ehden – Aaintourine; 14: Aaintourine; 15: Haouqa II; 16: Haouqa I; 17: Haouqa III; 18: Blaouza II; 19: Blaouza I.

(Figs 1 [locality 3], 2A, 3A) was discovered by Dany Azar in 2009 and is situated in the East of Qartaba near a cliff overhanging the valley of Janneh. The amber (translucent to transparent orange) is found as tiny droplets, less than 1 cm wide, in lens of lignite located in laterite on the top of a basaltic deposit.

HARISSA: (34°12.323'N; 35°57.080'E); Mouhafazet Loubnan Esh-Shemali (Governorate of North Lebanon), Caza (District) El-Batroun, Central Lebanon. The outcrop (Figs 1 [locality 5], 2B, 4A) was discovered by Dany Azar and Raymond Gèze in 2009 and is situated in the south-east of the Arz Tannourine (Cedar of Tannourine) reserve, on a small rocky road above the reserve's access point, near a small basin of water. The amber (translucent dark orange to creamy yellow) is found as small droplets, mostly less than 0.5 cm wide, in lens of lignite and altered pyrite, located in laterite on the top of a complex basaltic deposit.

HADATH EL-JOUBBEH: (34°13.828'N; 35°55.220'E); Mouhafazet Loubnan Esh-Shemali (Governorate of North Lebanon), Caza (District) Bcharreh, Northern Lebanon. The outcrop (Figs 1 [locality 8], 5A) was discovered by Dany Azar and Raymond Gèze in 2009 and is situated in the northern part of the cedar reserve of Tannourine in the Hadath El-Joubbeh territories, the southern part of the village. The amber (Fig. 5B) (translucent red to orange) is found as relatively large pieces (approximately 1–2 cm wide), in lignite and grey clay lenses corresponding to paleo-channels, located in a laterite and complex basaltic deposit.



Figure 2. (A) Outcrop of Qartaba. (B) Outcrop of Harissa. This figure is published in color in the online version.

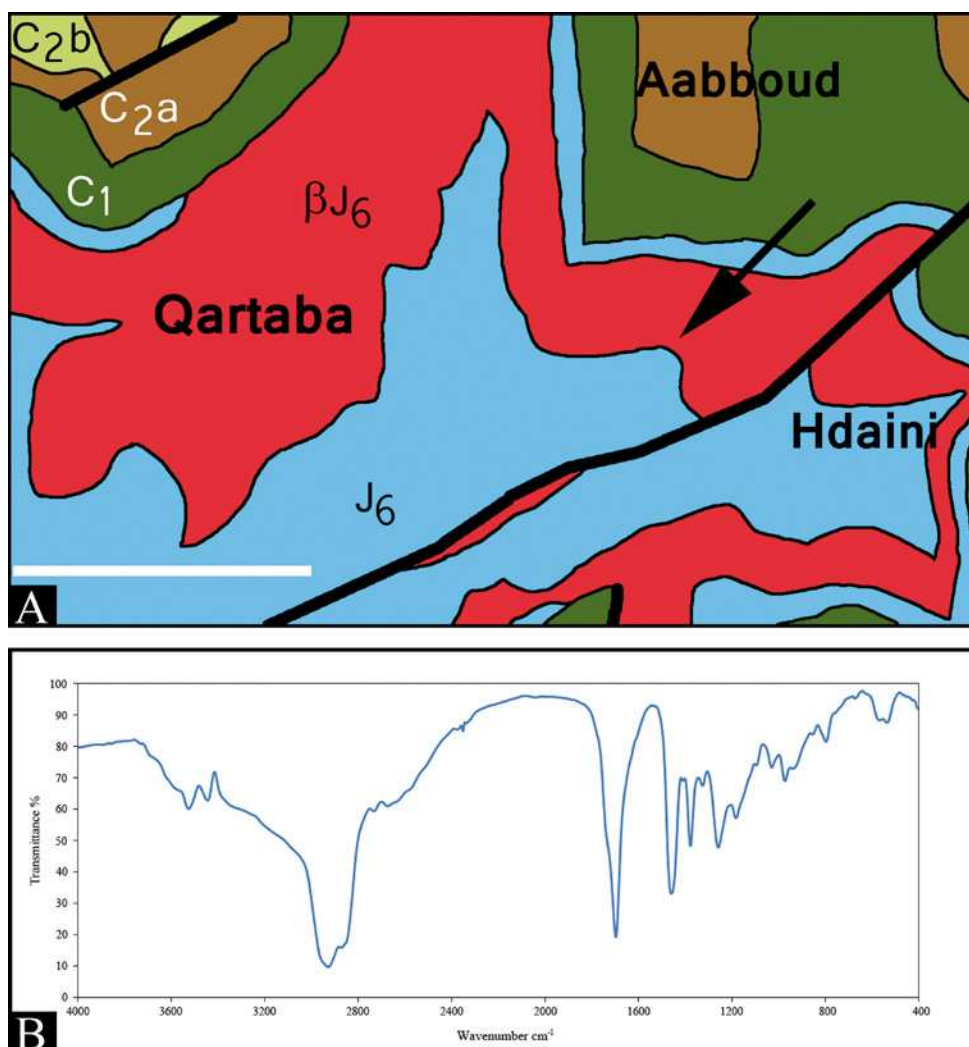


Figure 3. (A) Geological map of the outcrop of Qartaba [J_6 = Kimmeridgian; βJ_6 = Volcanic Kimmeridgian; C1 = Neocomian; C2a = Lower Aptian; C2b = Late Aptian; thickened lines represent faults; scale bar = 1 km]. (B) FTIR spectrum of the amber of Qartaba.

BLAOUZA: (34°15.896'N; 35°56.912'E); Mouhafazet Loubnan Esh-Shemali (Governorate of North Lebanon), Caza (District) Bcharreh, northern Lebanon. The outcrop (Blaouza II) (Figs 1 [locality 18], 7A, 8A) was discovered by Dany Azar, Raymond Gèze, Youssef Nohra and Sibelle Maksoud in 2011 and is situated on the left main road side when going from Bcharreh toward Ehden. This outcrop is different from the one described in Azar et al. (2010) (Blaouza I) (Fig. 1 [locality 19]) located at (34°15.562'N; 35°57.401'E) which is now completely destroyed, as construction was built over it (Azar et al., 2010). The amber (Fig. 7B, translucent yellow) is found as very tiny pieces in lignite located in a basaltic deposit. This site was a mine

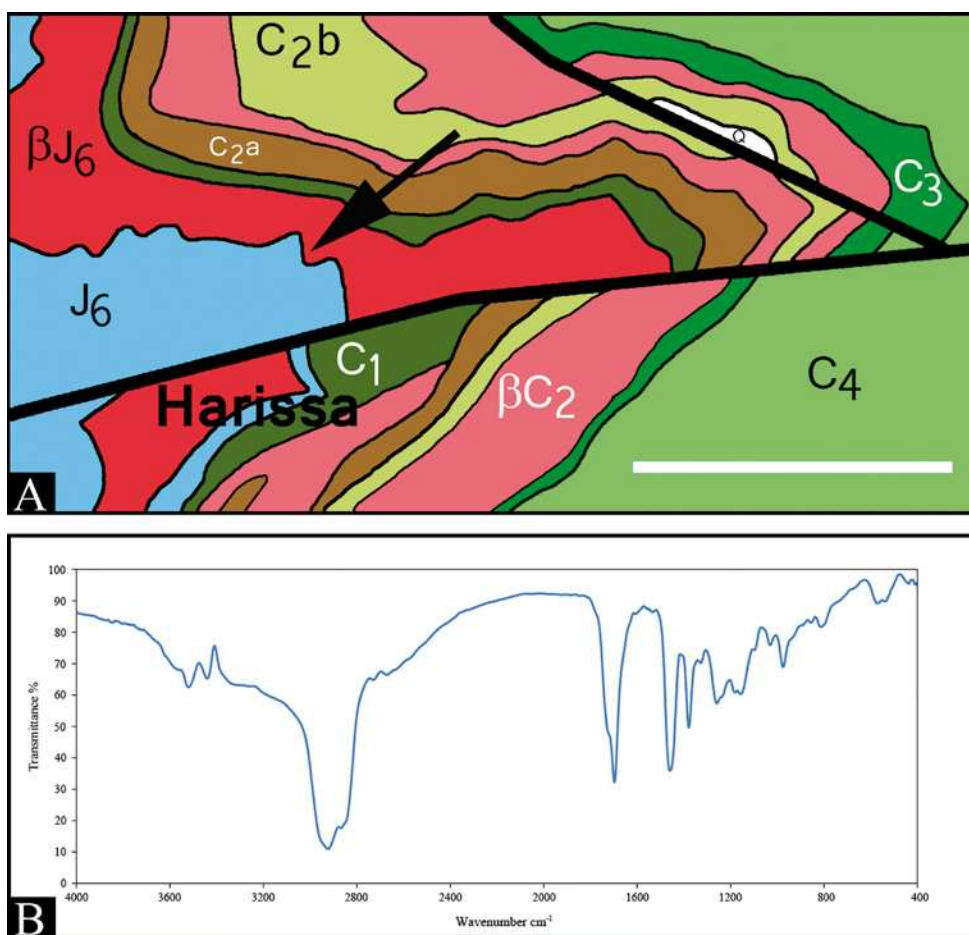


Figure 4. (A) Geological map of the outcrop of Harissa [J_6 = Kimmeridgian; βJ_6 = Volcanic Kimmeridgian; C_1 = Neocomian; C_2a = Lower Aptian; C_2b = Late Aptian; βC_2 = Volcanic Aptian; C_3 = Albian; C_4 = Cenomanian; Q = Quaternary; thickened lines represent faults; scale bar = 1 km]. (B) FTIR spectrum of the amber of Harissa.

exploited for lignite in the '40s, during the French protectorate of the Lebanese territories.

QNAIOUER: (34°16.143'N; 35°55.591'E); Mouhafazet Loubnan Eh-Shemali (Governorate of North Lebanon), Caza (District) Bcharreh, northern Lebanon. The outcrop (Figs 1 [locality 11], 9A, 10A) was discovered by Raymond Gèze in 2009 and is situated in the northern part of the village of Qnaiouer, overhanging the Wady Kannoubine (Kadisha Valley). The amber (Fig. 9B) (translucent creamy yellow) is found as tiny droplets, in lignite, located in laterite and a complex basaltic deposit.

HAOUQA: (34°16.179'N; 35°56.840'E); Mouhafazet Loubnan Esh-Shemali (Governorate of North Lebanon), Caza (District) Zgharta, Northern Lebanon. The outcrop (Haouqa II) (Figs 1 [locality 15], 11A, 12A) was discovered by Dany Azar, Raymond



Figure 5. (A) Outcrop of Hadath El-Joubbeh. (B) Amber from the outcrop of Hadath El-Joubbeh. Coin diameter = 24 mm. This figure is published in color in the online version.

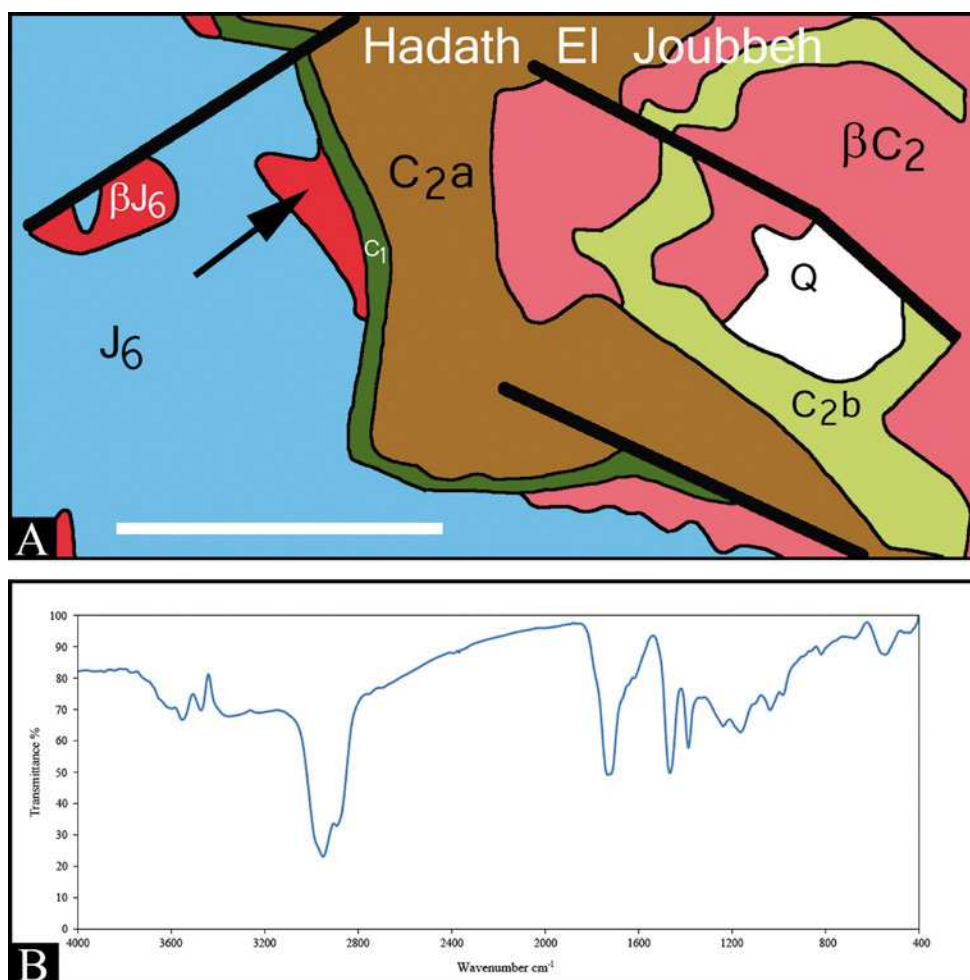


Figure 6. (A) Geological map of the outcrop of Hadath El-Joubbeh [J6 = Kimmeridgian; βJ_6 = Volcanic Kimmeridgian; C1 = Neocomian; C2a = Lower Aptian; C2b = Late Aptian; βC_2 = Volcanic Aptian; Q = Quaternary; thickened lines represent faults; scale bar = 1 km]. (B) FTIR spectrum of the amber of Hadath El-Joubbeh.

Gèze, Youssef Nohra and Sibelle Maksoud in 2011 and is situated in the village of Haouqa beneath the left side of the main road leading from Bcharreh toward Ehden. This outcrop is different from the one described by Azar et al. (2010) (Haouqa I) (Fig. 1 [locality 16]) located at (34°16.219'N; 35°56.906'E). The new Haouqa outcrop is located on the opposite side of the Valley of Wady Kannoubine facing the village of Qnaïouer. The amber (Fig. 11B) (translucent yellow) is found as very tiny pieces, in lens of lignitic laterite with well-preserved pyrite, located in a complex volcanic deposit. A third outcrop (Haouqa III) (Figs 1 [locality 17], 13A, 14A) also was discovered in Haouqa by the same group and is located at (34°16.162'N; 35°57.019'E), with the same type of amber deposition as the previous site. The amber (Fig. 13B) was found in lateritic lignite located on the top of basaltic deposit.



Figure 7. (A) Outcrop of Blaouza II. (B) Amber from the outcrop of Blaouza II. Coin diameter = 24 mm. This figure is published in color in the online version.

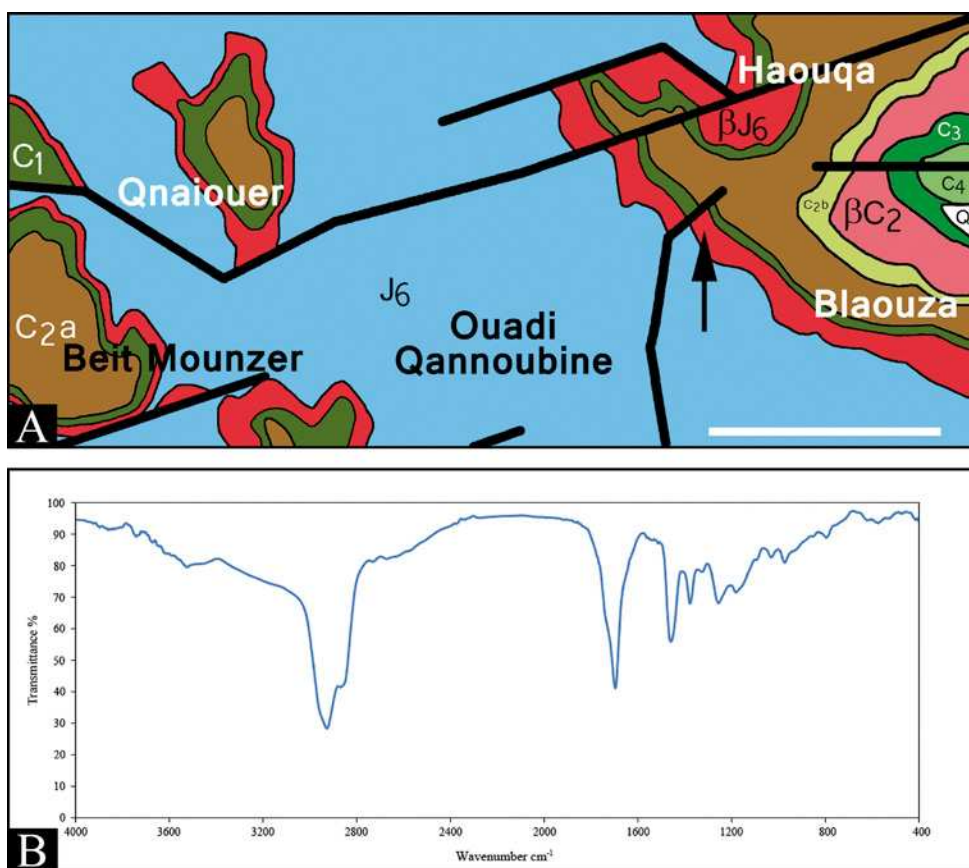


Figure 8. (A) Geological map of the outcrop of Blaouza II [J6 = Kimmeridgian; β J6 = Volcanic Kimmeridgian; C1 = Neocomian; C2a = Lower Aptian; C2b = Late Aptian; β C2 = Volcanic Aptian; C3 = Albian; C4 = Cenomanian; Q = Quaternary; thickened lines represent faults; scale bar = 1 km]. (B) FTIR spectrum of the amber of Blaouza II.

EHDEN: Mouhafazet Loubnan Esh-Shemali (Governorate of North Lebanon), Caza (District) Zgharta, Northern Lebanon. In this region there are 3 outcrops. All three amber sites (Fig. 1 [localities 12, 13, 14]) were discovered by Dany Azar and Raymond Gèze in 2009. The first outcrop (Ehden (Mantra)) (Figs 1 [locality 12], 15A, 16A) is situated in the west of the village of Ehden, in a locality named Mantra (34°17.680'N; 35°56.163'E), on the right side of the main road leading from Ehden toward Bcharreh. Just above the outcrop there is an old stone quarry, which has helped in revealing the amber deposit from this region. The amber (Fig. 15B) (translucent dark orange to transparent yellow) is found as relatively large pieces (approximately 1–2 cm in diameter) in lignite located in a basaltic deposit.

The second outcrop (Ehden – Aaintourine) (Figs 1 [locality 13], 17A, 18A) is also situated west of the village of Ehden, just before attempting the beginning of Aaintourine village, beneath a local church (34°17.678'N; 35°56.387'E). This site might be the continuity of the first outcrop in Mantra, located just above it. At this



Figure 9. (A) Outcrop of Qnaiouer. (B) Amber from the outcrop of Qnaiouer. Coin diameter = 24 mm. This figure is published in color in the online version.

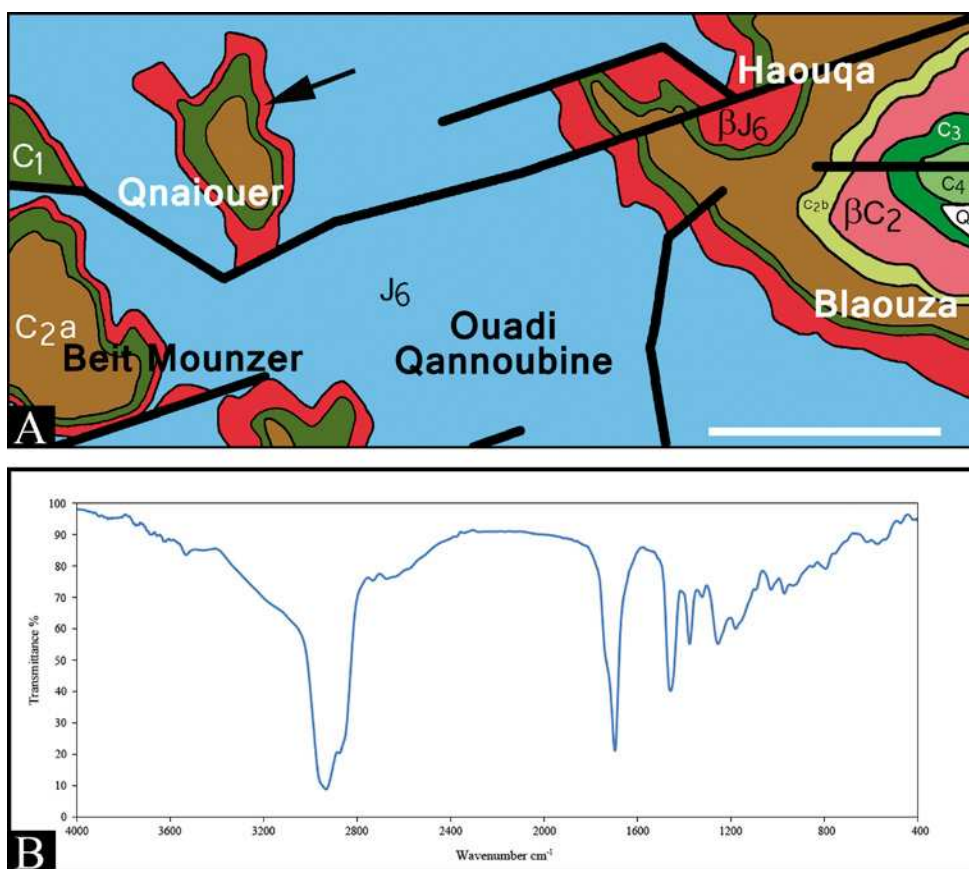


Figure 10. (A) Geological map of the outcrop of Qnaiouer; [J6 = Kimmeridgian; βJ_6 = Volcanic Kimmeridgian; C1 = Neocomian; C2a = Lower Aptian; C2b = Late Aptian; βC_2 = Volcanic Aptian; C3 = Albian; C4 = Cenomanian; Q = Quaternary; thickened lines represent faults; scale bar = 1 km]. (B) FTIR spectrum of the amber of Qnaiouer.

outcrop, a direct contact is visible between the volcanic Kimmeridgian βJ_6 (with amber) and the above Neocomian sandstone (symbolized as C1). The amber (Fig. 17B) (translucent to transparent orange to yellow) is found as large pieces in lignite, located directly on a complex volcanic material.

The third outcrop (Aaintourine) (Figs 1 [locality 14], 19A, 20A) is at the beginning of Aaintourine village on the road leading from Ehden to Aaintourine (34°17.517'N; 35°56.663'E). The outcrop is located on the left side of a small road, before the first houses of Aaintourine. The amber (Fig. 19B) (translucent red to orange and transparent yellow) is found in exceptional large pieces (approximately 3–5 cm in diameter) in lignite and dark clay mixed with laterites, located on basaltic deposit.

FTIR spectrometer

For the infrared analysis, 0.2 mg of amber (from each outcrop) was crushed and mixed with KBr (FTIR grade; Merck, Germany) and pellets were prepared using a



Figure 11. (A) Outcrop of Haouqa II. (B) Amber from the outcrop of Haouqa II. Coin diameter = 24 mm. This figure is published in color in the online version.

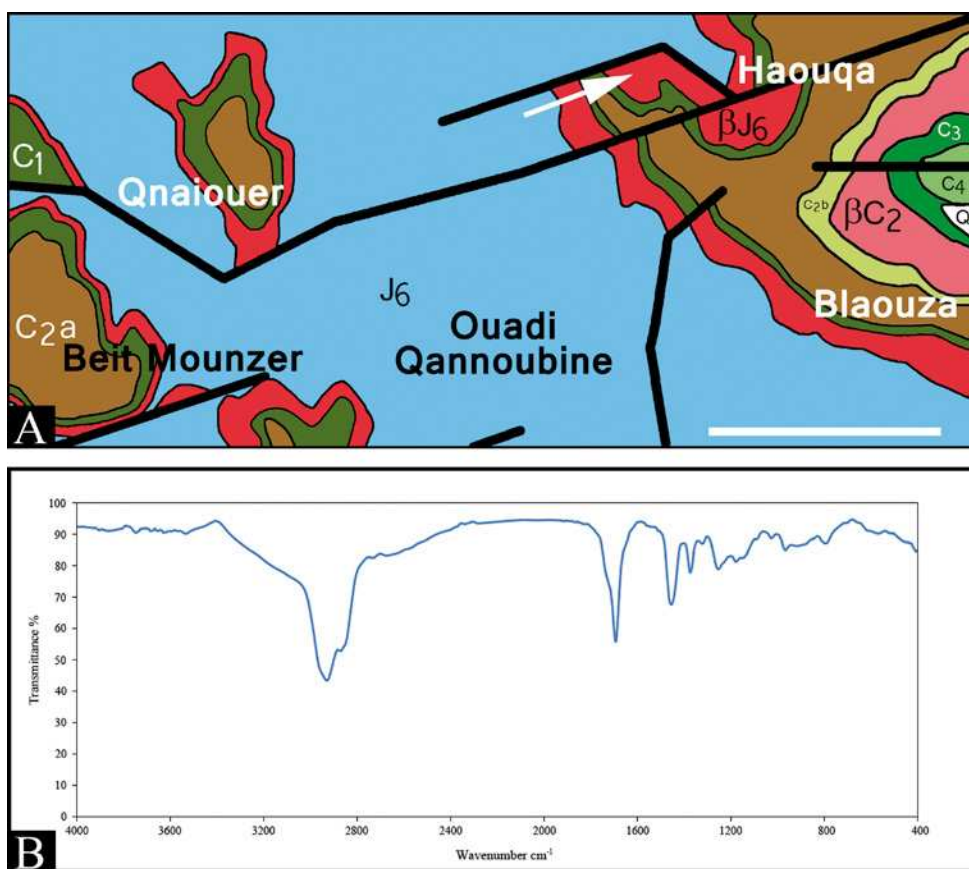


Figure 12. (A) Geological map of the outcrop of Haouqa II; [J6 = Kimmeridgian; βJ6 = Volcanic Kimmeridgian; C1 = Neocomian; C2a = Lower Aptian; C2b = Late Aptian; βC2 = Volcanic Aptian; C3 = Albien; C4 = Cenomanian; Q = Quaternary; thickened lines represent faults; scale bar = 1 km]. (B) FTIR spectrum of the amber of Haouqa II.

manual press. Transmission Fourier-Transform InfraRed (FTIR) spectroscopy was performed with a Bruker IFS 55 spectrophotometer. The spectrum was acquired between 4000 and 400 cm^{-1} range with 40 scans collected at 4 cm^{-1} resolution.

Results

The FTIR spectra of the analyzed amber from different outcrops are given in Figs 3B, 4B, 6B, 8B, 10B, 12B, 14B, 16B, 18B, 20B, and 21. Transmittance peaks at the wavelengths 3400 cm^{-1} and at 2955 cm^{-1} , 2865 cm^{-1} and 2925 cm^{-1} corresponds respectively to O-H stretching in phenolic and aliphatic compounds, to C-H asymmetric and symmetric stretching in CH_2 and C-H asymmetric stretching in CH_3 . Thus an aliphatic dominance is identified in these fossil resins. In these transmittance FTIR spectra, carbonyl (C=O) functional groups can be detected over the range of 1725–1680 cm^{-1} .



Figure 13. (A) Outcrop of Haouqa III. (B) Amber from the outcrop of Haouqa III. Coin diameter = 24 mm. This figure is published in color in the online version.

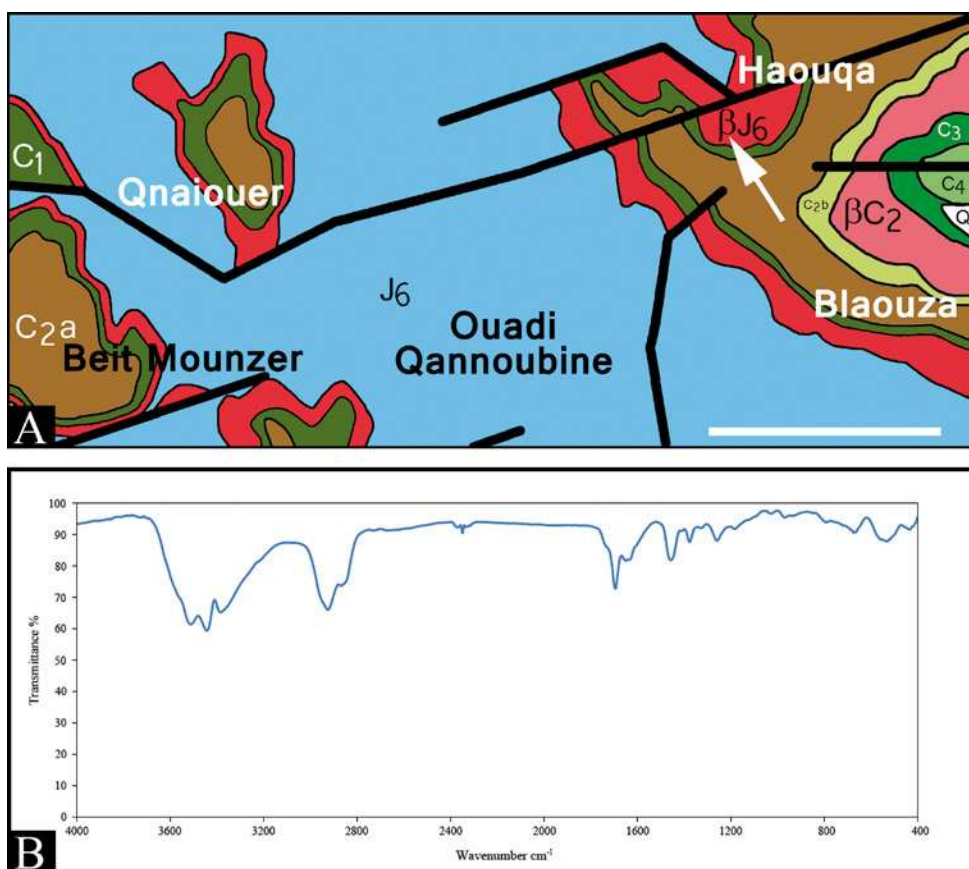


Figure 14. (A) Geological map of the outcrop of Haouqa III; [J6 = Kimmeridgian; β J6 = Volcanic Kimmeridgian; C1 = Neocomian; C2a = Lower Aptian; C2b = Late Aptian; β C2 = Volcanic Aptian; C3 = Albian; C4 = Cenomanian; Q = Quaternary; thickened lines represent faults; scale bar = 1 km]. (B) FTIR spectrum of the amber of Haouqa III.

The peaks observed at this range of wavelength is related to the stretching vibration of the C=O in free COOH groups, esters, and secondary amides. Also, the C=O functional groups are detected at the range of 1600–1540 cm^{-1} resulting an asymmetrical stretching in COOH groups and in carboxylate complex groups. The 1455 cm^{-1} and 1377 cm^{-1} bands reflect the OH deformation in phenolic groups and a contribution of C-H deformation in alkenes groups, and C-N stretching in amines. The peaks intensities are relatively quite similar in all the 10 spectra. All these detected functional groups indicate the large dominance of the aliphatic chains in the chemical constitution of the Jurassic amber, with a contribution of phenolic compounds and some amide.

Discussion

All 10 FTIR spectra of the different amber pieces present a high rate of similarity between them, concerning the major peaks described before. In the so called signature



Figure 15. (A) Outcrop of Ehden (Mantra). (B) Amber from the outcrop of Ehden (Mantra). Coin diameter = 24 mm. This figure is published in color in the online version.

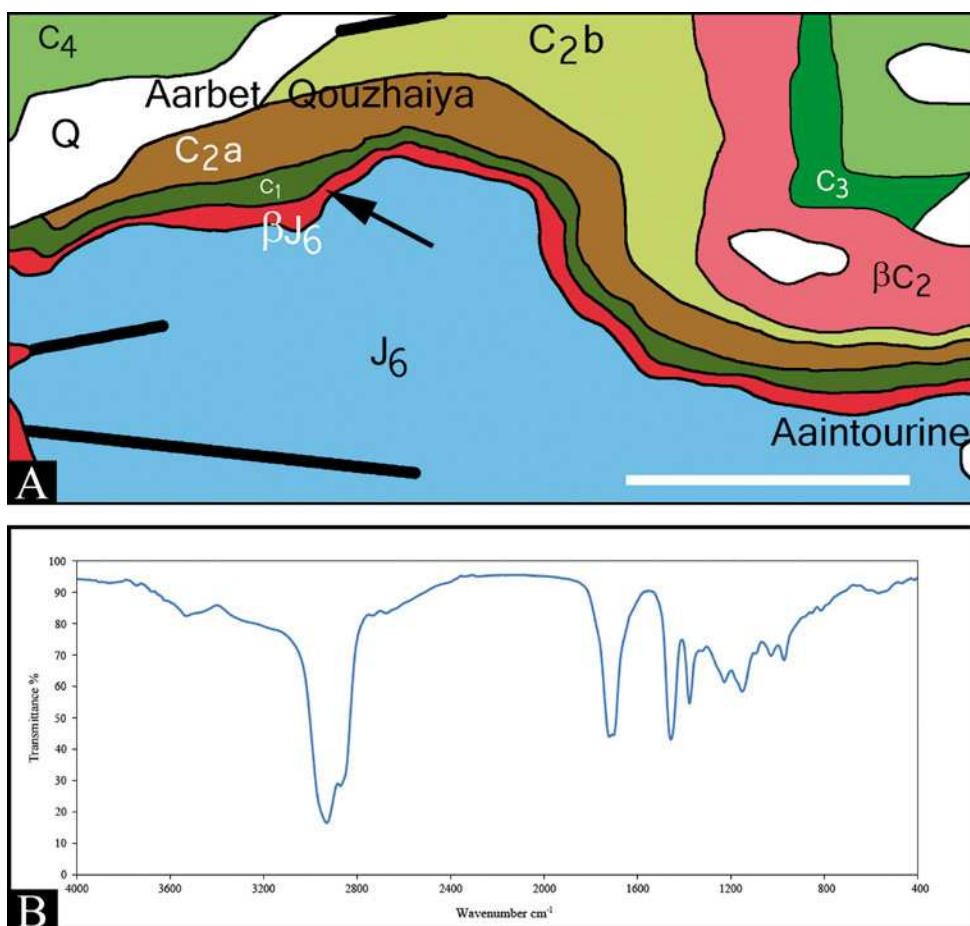


Figure 16. (A) Geological map of the outcrop of Ehden (Mantra); [J₆ = Kimmeridgian; βJ₆ = Volcanic Kimmeridgian; C₁ = Neocomian; C_{2a} = Lower Aptian; C_{2b} = Late Aptian; βC₂ = Volcanic Aptian; C₃ = Albian; C₄ = Cenomanian; Q = Quaternary; thickened lines represent faults; scale bar = 1 km]. (B) FTIR spectrum of the amber of Ehden (Mantra).

area (1800 – 400 cm⁻¹) slight differences can be observed between the studied spectra. Moreover, at the wavelength of 3400 cm⁻¹, 2955 cm⁻¹, 2865 cm⁻¹ and 2925 cm⁻¹, peaks are nearly detected in all the amber outcrops in the world, whatever was its origin or age (Grimaldi et al., 1989; Nicholas et al., 1993; Alonso et al., 2000; Roghi et al., 2006; Pakutinskiene et al., 2007; Peñalver et al., 2007; Teodor et al., 2009; Engelbrecht et al., 2010).

The similarity of the obtained spectra can be explained probably by the same botanical origin of the resin at that time (Kimmeridgian, nearly 150 Ma). However, even though the amber sites are near to each other, the taphonomy of the fossilized resin in each of the localities can differ, thus the slight differences observed at the range 1800 – 400 cm⁻¹ can be explained.



Figure 17. (A) Outcrop of Ehden – Aaintourine. (B) Amber from the outcrop of Ehden – Aaintourine. Coin diameter = 24 mm. This figure is published in color in the online version.

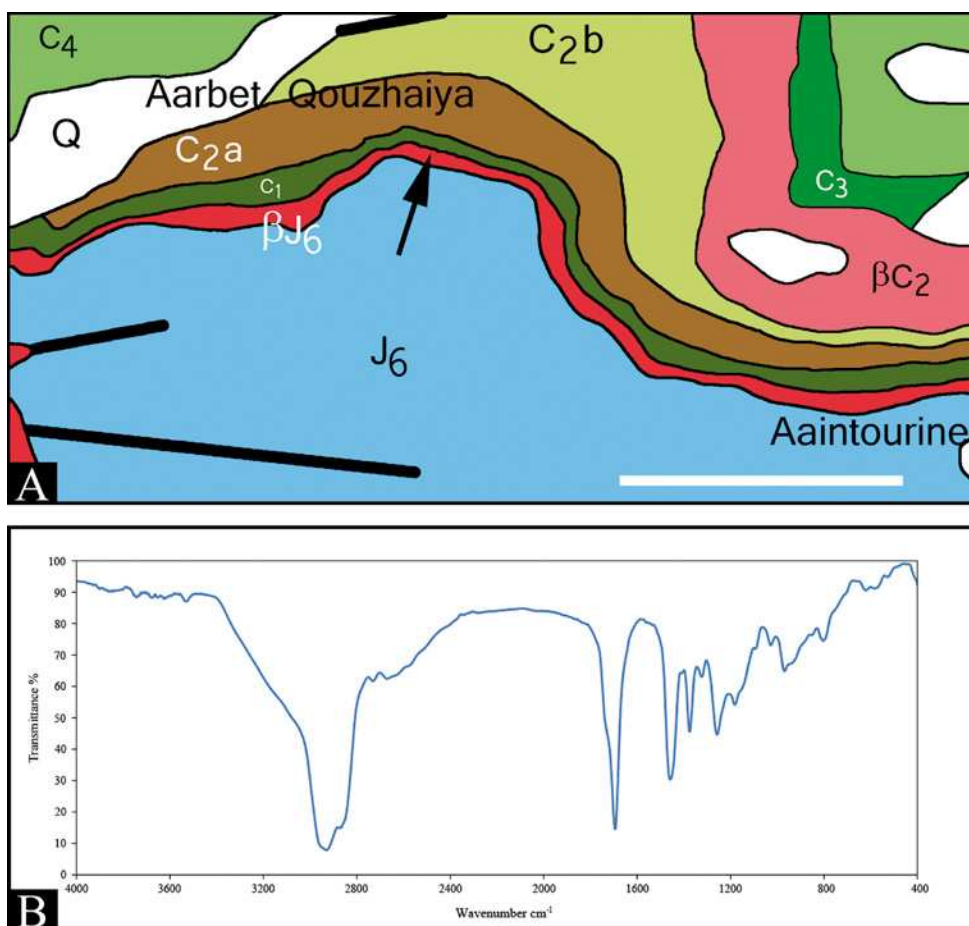


Figure 18. (A) Geological map of the outcrop of Ehden – Aaintourine; [J6 = Kimmeridgian; βJ6 = Volcanic Kimmeridgian; C1 = Neocomian; C2a = Lower Aptian; C2b = Late Aptian; βC2 = Volcanic Aptian; C3 = Albian; C4 = Cenomanian; Q = Quaternary; thickened lines represent faults; scale bar = 1 km]. (B) FTIR spectrum of the amber of Ehden – Aaintourine.

The Infrared spectra of the Jurassic amber are also comparable to the one obtained from a Lebanese Lower Cretaceous outcrop (Fig. 21 [spectrum 11]), the one of Hammana / Mdeyrij. We notice that, not only the rate of similarity is important between the Jurassic ambers, but also with the Lower Cretaceous one. Which lead us to conclude that most likely we have the same vegetal group origin of the corresponding resins, adding to this the stability of paleoenvironment at these two geological stages (Late Jurassic and Lower Cretaceous).

According to Azar et al. (2010), the spectra of Lebanese amber (Jurassic and Cretaceous) are comparable with those that originated from recent *Araucariaceae* (Langenheim and Beck, 1965; Langenheim, 1969). But, most of the infrared spectra of amber from all over the world present more or less similar aspects and profiles. This may lead not only to an *araucarian* origin but to any type of resinous group.



Figure 19. (A) Outcrop of Aaintourine. (B) Amber from the outcrop of Aaintourine. Coin diameter = 24 mm. This figure is published in color in the online version.

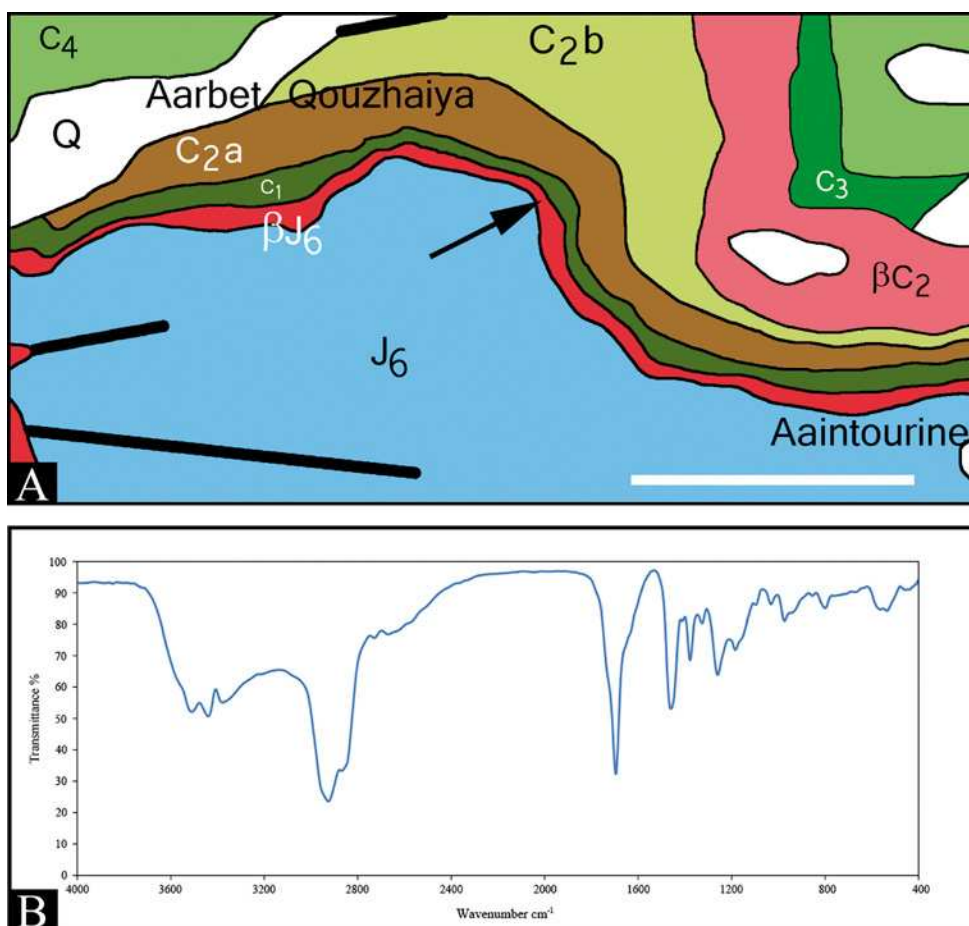


Figure 20. (A) Geological map of the outcrop of Aaintourine; [J6 = Kimmeridgian; βJ6 = Volcanic Kimmeridgian; C1 = Neocomian; C2a = Lower Aptian; C2b = Late Aptian; βC2 = Volcanic Aptian; C3 = Albian; C4 = Cenomanian; Q = Quaternary; thickened lines represent faults; scale bar = 1 km]. (B) FTIR spectrum of the amber of Aaintourine.

Hence, the Infrared analyses alone are not so precise in helping to reveal the origin of the amber. The question of the origin can be resolved by studying the fossil wood (xylogy) which is found associated with the amber, or the palynomorphs found within the same location. Nevertheless here too there are several difficulties to reveal the botanical origin of amber, as palynomorphs could be carried for long distances by wind or water and deposited in the same area where the fossilized resin is found, and as for the wood taxonomy (when this later is present and not so carbonized to allow its study), different nomenclature could be given to the same material depending on the researchers. A third possibility for revealing the botanical origin is by using the study of leaves epidermis (when leaves are present in sediment and carbonization is not very advanced), but here too this case is not frequent at all (even somehow exceptional), and could be applied only to some outcrops where amber is in its primary deposition.

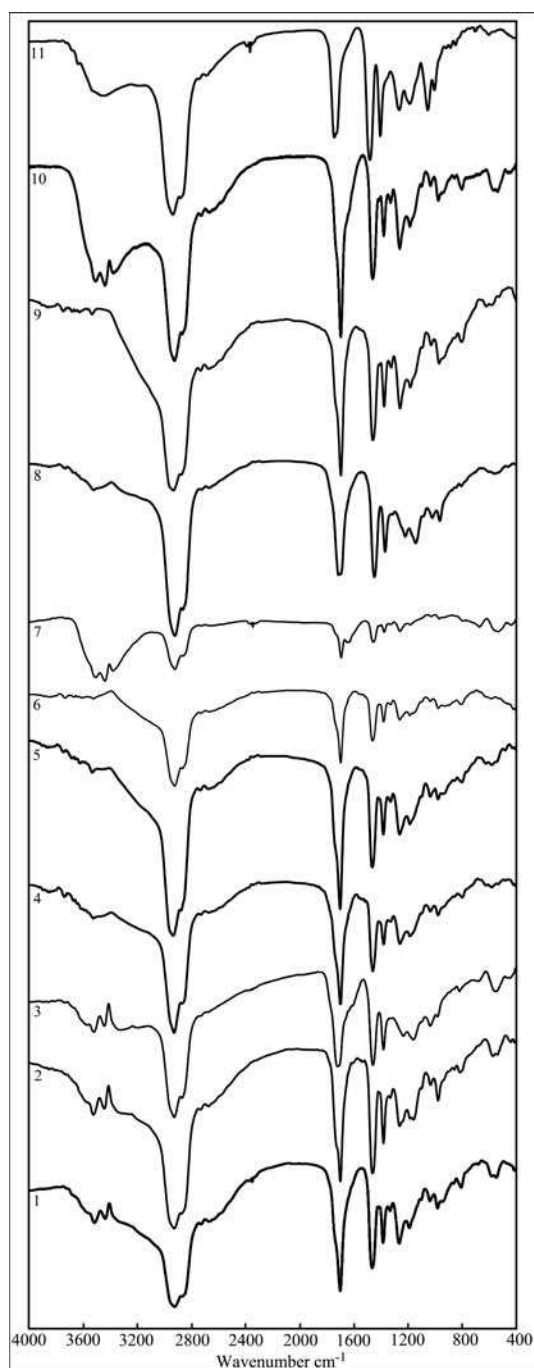


Figure 21. FTIR transmittance spectra, 1-10: Jurassic amber spectra, 11: Cretaceous amber spectrum of Hammana. (1) Spectrum of amber of Qartaba; (2) spectrum of amber of Harissa; (3) spectrum of amber of Hadath El-Joubbeh; (4) spectrum of amber of Blaouza II; (5) spectrum of amber of Qnaiouer; (6) spectrum of amber of Haouqa II; (7) spectrum of amber of Haouqa III; (8) spectrum of amber of Ehden (Mantra); (9) spectrum of amber of Ehden – Aaintourine; (10) spectrum of amber of Aaintourine.

According to the xylology, two origins could be proposed (depending on workers) for the Lower Cretaceous Lebanese amber (which might be the same for the Late Jurassic ones): Araucariaceae (*Araucaroxydon* sp.), or Cheirolepidiaceae (Protopodocarpoxylon sp.). The study of the epidermal structure would suggest another botanical group with cycads affinity or even a new fossil family.

Conclusion

The Late Jurassic outcrops herein studied in addition to the first nine outcrops described by (Azar et al., 2010), makes Lebanon the most abundant region with Late Jurassic amber locations, with a total of 19. Abundance of amber localities in this country in both Jurassic and Cretaceous makes Lebanon “incontournable” for studying the paleoenvironment for these extremely important epochs. Researches are currently on going for Jurassic Lebanese amber; we hope one day to find some arthropod inclusions in it, as to date only a few fungi have been recovered within this precious material.

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